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Phase change ink colorants and phase change inks produced therefrom.

This invention relates to modified phase change ink compatible colorants which comprise a phase change ink soluble complex of (a) a tertiary alkyl primary amine and (b) dye chromophores, i.e., materials that absorb light in the visible wavelength region to produce color having at least one pendant acid functional group in the free acid form (not the salt of that acid). These modified colorants are extremely useful in producing phase change inks when combined with a phase change ink carrier, even though the unmodified dye chromophores have limited solubility in the phase change ink carrier. Thin films of uniform thickness of the subject phase change ink compositions which employ the modified phase change ink colorants exhibit a high degree of lightness and chroma. The primary amine-dye chromophore complexes are soluble in the phase change ink carrier and exhibit excellent thermal stability.

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A further physical property employed to evaluate the durability of phase change inks and ink carrier compositions is offset transfer. This property is evaluated by a blocking (offsetting) test which determines whether the phase change ink printed on a substrate will adhere to an adjacent substrate at ambient or elevated temperatures when the printed products are stacked one on top of the other. The blocking test is conducted by printing samples of the phase change ink produced from the carrier composition on to a paper or thin film substrate and placing same in a manila folder under a one pound piece of aluminum, 8.5 inches wide and 11 inches long, which evenly distributes the weight of a 10 pound block. These printed samples reside in an oven for 24 hours at a constant temperature of 70°C. Print samples of the phase change ink were subjected to the above described blocking test and showed no signs of offsetting, spreading or adhesion.

Another important property of phase change inks is viscosity. The viscosity of the molten ink must be matched to the requirements of the ink jet device and optimized versus other physical properties of the ink. For purposes of this invention, the viscosity of the phase change ink is measured on a Ferranti-Shirley Cone Plate Viscometer with a large cone. It is preferred that the viscosity of the phase change ink carrier composition, at 140°C, and in turn the ink composition of this invention, is from about 5 to 30 centipoise, and more preferably from about 10 to 20 centipoise, most preferably from about 12 to 14 centipoise.

The following Examples, illustrate the invention by way of example only.

EXAMPLE 1

This example demonstrates a method of producing the preferred phase change ink colorant composition employed in producing the phase change ink composition of EXAMPLE 2 below (Method A) and an alternate method for forming the phase change ink colorant in situ during the phase change ink formation process (Method B).

(Method A) In a typical preparation of the acid form of Acid Red 52, 5.0g. of the water soluble dye (C.I. Acid Red 52) were dissolved in 100 mls. deionized water at room temperature and filtered through Whatman number 40 filter paper. To this solution were added 3 mls. of concentrated sulfuric acid with stirring. A green, crystalline precipitate of the acid form of the dye formed immediately. The acidified mixture was chilled to 5-10 deg C overnight to complete the precipitation, filtered through Whatman number 541 paper, the green precipitate washed three times with 20 ml. portions of cold water to remove mineral salts and the product dried under vacuum. The yield of the free acid form of C.I. Acid Red 52 colorant amounted to 4.8 g.

The amine complex of the free acid form of the dye is formed by an association of the dye with the Primene 81-R (Rohm and Haas Texas Inc.). In a typical preparation, 5.0 g. Neolan Red E-XB 400 FA (free acid form of C.I. Acid red 52 produced by Ciba-Geigy) were mixed with 1.75 grams Primene 81-R (avg. molecular wt. = 213) in 50 ml of methanol, and the solution stirred 30 minutes at room temperature. The solvent was removed using a rotary evaporator to yield a dark green syrup. Removal of the last traces of methanol solvent under a rough pump vacuum produced 6.5 grams of lustrous green crystals of the Primene complex. This material, referred to as Rhodamine P, is then combined with a phase change ink carrier composition as provided in EXAMPLE 2.

(Method B) The Primene complex of the free acid form of C.I. Acid Red 52 colorant may also be formed in situ. In a typical procedure, 1.4kg. of the phase change ink carrier composition described in EXAMPLE 2 is warmed to 100-120 deg C with stirring in a closed container. To this is added 3.2 g. (0.23% by weight) of Primene 81-R, followed immediately by the addition of 8.4 grams (0.60 % by weight) of the free acid form of C.I. Acid Red 52 colorant. Stirring was continued another 5 minutes. At the end of this time, the ink preparation was forced filtered with a 30 psig nitrogen pressure through a heated Mott filter apparatus 6.0 cm i.d. by 42 cm. length. A 0.2 micron nylon membrane filter supported on a 40 micron stainless steel disc serves as the filter element.

EXAMPLE 2

This example demonstrates a method of producing a preferred phase change ink by combining the preferred phase change ink colorant composition of EXAMPLE 1, Method A and a preferred phase change ink carrier composition.

More specifically, solid phase change ink ingots of the subtractive primary colors were produced as follows: 56 grams of Kemamide S-180 (Witco Corporation), 30 grams of Unirez X37-523-235 (a Dimer acid-based tetra-amide material manufactured by Union Carbide and formed by the reaction of one mole of dimer acid, two moles of ethylene diamine, and two moles of stearic acid), 10 grams of Arakawa KE-311 Resin,

and 0.1 grams of Naugard 524 were melted at 110 degrees C. When the mixture was completely molten and uniform, 0.75 grams of the Rhodamine P dye (the free acid form of C.I. Acid Red 52 colorant complexed with 1 equivalent of Primene 81-R) were added to the molten ink carrier and stirred at 100 degrees C. for about one hour. After a homogeneous solution of the material was achieved, the molten ink was filtered through a heated filter. The filtrate was poured into molds and allowed to solidify. Solid ink ingots of the magenta colorant were formed.

The above procedure was repeated with the other primary colorants required for ink jet color printing being substituted for the magenta colorant as follows: 0.9 grams of Orasol Yellow 4GN (C.I. Solvent Yellow 146 from Ciba-Geigy) to produce yellow solid ink ingots; 1.0 grams of Savinyl Blue GLS (C.I. Solvent Blue 44 from Sandoz) to produce cyan solid ink ingots; and 1.4 grams of Savinyl Black RLS-IJ (C.I. Solvent Black 45 from Sandoz) to produce solid black ink ingots.

EXAMPLE 3

This example demonstrates the high chroma (C^*_{ab}), and high ink thermal oxidation stability of the phase change ink compositions produced through the use of the phase change ink colorants of the present invention.

COLOR MEASUREMENTS OF PRINT SAMPLES

The reflectance spectra test data for the primary and secondary colors are listed in Table 1 below. (Measurement conditions were: Illuminate C, 2 degree observer, small area view, specular included, wavelength interval 10 nm.)

Table A

Color	L*	A*	B*	DL*	Da*	Db*	DC*ab	Hab
Black	23.69	1.86	-2.57	-69.68	0.95	-0.58	0.99	305.82
Cyan	58.03	-27.36	-39.38	-35.34	-28.26	-37.39	45.77	235.21
Magenta	55.40	85.43	-22.78	-37.96	84.52	-20.79	86.23	345.07
Yellow	89.51	-17.72	88.39	-3.85	-18.62	90.38	87.97	101.33
Red	53.44	65.71	40.07	-39.92	64.80	42.05	74.77	31.37
Green	54.67	-66.81	31.98	-38.70	-67.72	33.97	71.89	154.42
Blue	33.88	43.45	-48.42	-59.49	42.55	-46.43	62.88	311.91
Paper	93.37	.90	-1.99					

The phase change ink carrier composition and the magenta ink compositions of this invention have very high lightness (L^*) and chroma (C^*_{ab}) values.

INK THERMAL OXIDATION STABILITY TEST

In a typical test of the stability of a phase change ink composition, 800 grams of a molten ink sample was added to a one liter Erlenmeyer flask. A 23 cm Pasteur disposable borosilicate glass pipet is inserted into a two hole Teflon cap taped on the top of the flask, such that the pipet tip is about 1 cm off the bottom of the flask. Filtered air is blown through the pipet at the rate of 470 cc per minute. The flask is placed in an oven at 145 degrees C. The cooling effect of the air keeps the actual ink temperature at about 140 degrees C. The ink is heated and sparged typically between 120 to 140 hours.

Spectral strength of the phase change ink colorant in the ink is determined on a Perkin Elmer Lambda 3B Spectrophotometer. An acceptable colorant will have lost less than 10% of its spectral strength under the above vigorous conditions.

The phase change ink produced in accordance with the procedure outlined in EXAMPLE 2 was tested by the above procedure, and was found to have lost less than 10% of its spectral strength.

EXAMPLE 4

This example demonstrates the high degree of lightness (L^*) of the phase change ink carrier and ink composition, and the high chroma (C^*_{ab}) of the phase change ink composition of the present invention.

Two 2 inch square light transmissive glass plates were joined at opposite ends with a U.V. curable epoxy resin leaving the remaining opposite ends open. The plates were joined so that the plate faces were separated by a space of about 20 micron and were offset about 3/16 of an inch at the open ends to form entry lips. A sample of each of the yellow, magenta and cyan phase change ink ingots described in Example 1 were added to the space by placing it on one of the entry lips. The plates were then heated to a temperature of 106°C. At that temperature the ink became molten and flowed into the space formed between the plate faces by capillary action. Therefore, when the phase change ink cooled, a phase change ink of a substantially uniform thickness was produced. The transmission spectra test data for each primary color are listed in Table 1 below. (Measurement conditions were: Illuminate C, 2 degree observer, small area view, specular included, wavelength interval 10 nm.)

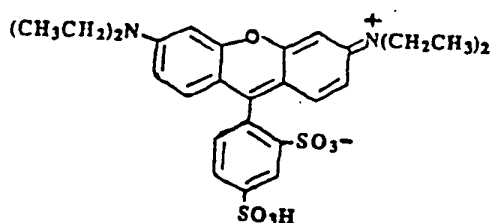
TABLE B

Sample	L*	a*	b*	C* _{ab}	h _{ab}
Glass only	92.34	-1.65	1.80	2.44	132.57
Glass with ink carrier	86.51	-0.64	4.54	4.58	98.03
Glass with cyan ink	75.48	-29.85	-17.18	34.44	209.91
Glass with magenta ink	56.01	69.12	-39.24	79.48	330.41
Glass with yellow ink	86.81	-14.66	55.04	56.96	104.91
Glass with black ink	19.45	7.48	-13.02	15.01	299.89

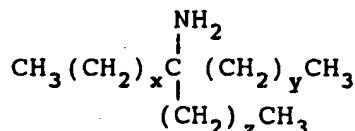
The ink carrier and the yellow, magenta and cyan ink compositions of this invention had relatively high lightness (L*) values, while the L* value of the black ink was relatively low high for the yellow, magenta and cyan inks of this invention. It should be readily apparent to those skilled in the art that the invention can be modified in arrangement and detail without departing from such principles.

Claims

1. A modified phase change ink composition comprising a modified phase change ink colorant in combination with a phase change ink carrier, said modified phase change ink colorant comprising the reaction product of (a) a tertiary alkyl primary amine and (b) dye chromophores having at least one pendant functional free acid group in the acid form, the dye chromophores, prior to the reaction with the tertiary primary amine, having a low degree of solubility in said phase change ink carrier, said phase change ink carrier being in a solid phase at ambient temperature and in a liquid phase at an elevated operating temperature, and thin films of uniform thickness of said modified phase change ink composition having a high degree of lightness, chroma and thermal stability.
2. A composition as claimed in Claim 1, wherein said dye chromophores, prior to the reaction with the tertiary primary amine, comprise C.I. Acid Red 52 dye, another C.I. Acid dye or a C.I. direct dye.
3. A composition as claimed in Claim 1 wherein said dye chromophores comprise a free acid derivative of a xanthene dye.
4. A composition as claimed in Claim 3 wherein the xanthene dye free acid derivative is represented by the formula:-



5. A composition as claimed in any preceding claim wherein said tertiary alkyl primary amine is represented by the formula:-



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wherein $X = 0 - 18$, $y = 0 - 18$, $z = 0 - 18$ and $x + y + z = 8$ to 18 .

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6. A composition as claimed in any preceding claim wherein said tertiary alkyl primary amine has a total of from 12 to 22 carbon atoms.

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7. A composition as claimed in any preceding claim which comprises a solvent-soluble magenta dye which exhibits an intense, saturated color and a high degree of thermal stability.

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8. A composition as claimed in any preceding claim wherein (i) the modified phase change ink colorant is a subtractive primary yellow color phase change ink and wherein a substantially uniform thin film of about 20 microns thickness of a subtractive primary yellow color phase change ink composition produced from said colorant has a C^*_{ab} value of at least about 40, (ii) the modified phase change ink colorant is a subtractive primary magenta color phase change ink and wherein a substantially uniform thin film of about 20 microns thickness of a subtractive primary magenta color phase change ink composition produced from said colorant has a C^*_{ab} value of at least about 60; (iii) the modified phase change ink colorant is a subtractive primary cyan color modified phase change ink and wherein a substantially uniform thin film of about 20 microns thickness of a subtractive primary cyan color modified phase change ink composition produced from said colorant has a C^*_{ab} value of at least about 25; or (iv) the modified phase change ink colorant is a black color modified phase change ink and wherein a substantially uniform thin film of about 20 microns thickness of a black color modified phase change ink composition produced from said colorant has an L^* value of not more than about 35, preferably not more than about 30.

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9. A composition as claimed in any preceding claim wherein thin films of uniform thickness of said ink composition are rectilinearly light transmissive.

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10. A phase change ink compatible colorant complex for combination with a phase change ink carrier, said complex being obtainable by reacting at least one tertiary alkyl primary amine with one or more dye chromophores having each at least one pendant functional free acid group and each chromophore in non-complexed form demonstrating poor solubility in said carrier.

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11. A phase change ink composition comprising a phase change ink carrier and a colorant complex as claimed in Claim 10.

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12. A process for producing a phase change ink composition as claimed in Claim 11 which process comprises either (i) combining the phase change ink carrier with said colorant complex to form said ink composition or (ii) combining the phase change ink carrier with said tertiary alkyl primary amine, combining the resulting mixture with the dye chromophore and allowing or causing the chromophore to undergo an in situ complexing reaction with said amine.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 262 821 (HEWLETT-PACKARD CO.) * claim 1 * -----	1	C09D11/00
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 JUNE 1993	Examiner BEYSS E.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	